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(71) Applicant: IDEMITSU PETROCHEMICAL COMPANY
LIMITED
No. 1-1, 3-chome, Marunouchi Chiyoda-ku
Tokyo(JP)

(72) Inventor: Misasa, Mitsugu
No. 9, 2-chome Kiyomidai-minami
Kisarazu-shi Chiba-ken(JP)

(72) Inventor: Hirayama, Ryoichi
No. 13-11, 1-chome Kogane-kiyoshigaoka
Matsudo-shi Chiba-ken(JP)

(74) Representative: SERJEANTS
25, The Crescent
Leicester, LE1 6RX(GB)

(54) Laminated materials.

(57) A laminated material comprises (A) a layer composed mainly of polyolefin, (B) a layer composed mainly of a saponified produce of an ethylenevinyl acetate copolymer, a polyamide resin or a polyester resin, (C) a vacuum deposited metallic layer, and (D) a layer composed mainly of a transparent thermoplastic resin. This laminated material has superior gas barrier properties, light-shielding properties, moisture resistance, etc. and is suitable for use as a packaging material.

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TITLE:- LAMINATED MATERIALS**DESCRIPTION**

The invention relates to laminated materials which are useful as wrapping materials or packaging materials for foodstuffs.

5 Aluminium and multi-layer plastics sheets have heretofore been used as food packaging materials; they are moulded by techniques such as stretch forming and thermoforming to produce food packaging containers. However, containers made of aluminium have disadvantages in that they are readily subject
10 to breakage or deformation during filling or transportation; in particular, such deformation leads to a serious reduction in product value since the deformed containers cannot be restored.

15 Multi-layer plastics sheets include those sheets made of polyolefins and polystyrenes. In addition, to increase the hygienic or decorative effect, those materials with an aluminium vacuum deposited layer laminated on the surface thereof have been

proposed. Although these laminated materials are sufficiently applicable for use as packaging materials, they suffer from disadvantages in that in producing various containers the surface becomes uneven and is readily scratched, and there cannot be obtained the decorative effect of the lustre of aluminium. Furthermore, they are inferior in

respect of gas barrier properties, light-shielding properties, heat resistance, and so forth. Another

type of laminated material which has been proposed is produced by laminating a multilayer consisting of a vacuum deposited metallic layer as an inner layer and a thermoplastic resin sheet as an outer layer on a soft type resin such as low density polyethylene by an extrusion lamination process.

These materials, when produced in combination with those sheets having high rigidity, suffer from disadvantages in that when they are treated under high temperature sterilizing conditions, the vacuum deposited metallic layer is scattered, and they become unsuitable for practical use. Thus, they are limited in their utilization.

The invention provides a laminated material comprising: (A) a layer composed mainly of polyolefin; (B) a layer composed mainly of a saponified product

of an ethylene-vinyl acetate copolymer, a polyamide resin or a polyester resin; (C) a vacuum deposited metallic layer; and (D) a layer composed mainly of a transparent thermoplastic resin.

5 Polyolefins which can be used in the preparation of layer A include polypropylene, copolymers of propylene and other monomers (e.g., α -olefin), high density polyethylene, medium density polyethylene, and low density polyethylene.
10 Polypropylene and high density polyethylene are preferred.

 Between layer A and layer B as described hereinafter may be sandwiched a layer of polyolefin modified with an unsaturated carboxylic acid or a
15 derivative of an unsaturated carboxylic acid. Polyolefins which may be used in the preparation of such modified polypropylenes include propylene homopolymer, block copolymers or random copolymers of propylene and other co-monomers (e.g., ethylene),
20 ethylene homopolymer, and copolymers of ethylene and other α -olefins. Unsaturated carboxylic acids which can be used include acrylic acid, methacrylic acid, maleic acid, fumaric acid, itaconic acid, crotonic acid, citraconic acid, sorbic acid,
25 mesaconic acid, and angelic acid. Their

derivatives include acid anhydrides, esters, amides, imides, and metal salts. Specific examples of such unsaturated carboxylic acid derivatives include maleic anhydride, itaconic anhydride, methyl acrylate, acrylamide, maleimide, and sodium acrylate.

5 Modification of polyolefin with unsaturated carboxylic acid or its derivative may be performed by any suitable procedure. For example, the polyolefin and maleic anhydride may be heated in
10 combination with a radical polymerization initiator in the presence or absence of a solvent to obtain the desired modified polyolefin. In this case, vinyl monomers such as styrene, or rubbers such as liquid
15 rubber and thermoplastic rubber may be added to the reaction system. The unsaturated carboxylic acid or its derivative content of the modified polypropylene is usually from 0.001 to 15% by weight and preferably from 0.005 to 10% by weight. The term "modified
20 polyolefin" as used herein also includes a mixture of modified polyolefin and unmodified polypropylene.

Layer B of the laminated material of the invention is a gas barrier resin layer. There is no limitation on the composition of the saponified
25 product of the ethylene-vinyl acetate copolymer.

However, for the best gas barrier and oil resistance properties, it is preferred to use products resulting from the saponification of ethylenevinyl acetate copolymers having an ethylene content of from 25 to 50 mole %, the degree of saponification being at last 93% and preferably at least 96%. Polyamide resins are linear synthetic polymers containing -CONH- linkages which are obtained by condensation of diamines and dicarboxylic acids, or self condensation of amino acids, or ring-open polymerization of lactams. Typical examples of the polyamide resins that can be used include 6-nylon (polycapramide), 6,6-nylon (polyhexamethylene adipamide), 6,10-nylon (polyhexamethylene sebacamide), 11-nylon (polyundecamide), and 12-nylon. Polyester resins are prepared by condensation of saturated dicarboxylic acids and glycols. Examples are polyethylene terephthalate produced from ethylene glycol and terephthalic acid; polyethylene terephthalate copolymers containing a saturated dibasic acid, such as phthalic acid, isophthalic acid, sebacic acid, adipic acid, azelaic acid, glutaric acid, succinic acid, and oxalic acid, as a copolymer component; polyethylene terephthalate copolymers containing a diol component, such as 1,4-dihydroxymethyl-

-cyclohexane, diethylene glycol, propylene glycol, or the like as a copolymer component; and their mixture.

Between layer B and layer C may be interposed, if desired, a layer of a synthetic resin. Synthetic resins which may be used for this purpose include polyethylene and polypropylene.

Layer C of the laminated material of the invention is a vacuum deposited metallic layer. Usually, aluminium is used to form layer C. However, zinc, chromium, nickel, gold, silver or other metals may be used depending on the intended purpose of the laminated material.

Layer D is composed mainly of a transparent thermoplastic resin. Preferably it is a non-stretched film. There is no limitation on the thermoplastics resin as used herein. For example, polyamides, polymethyl methacrylates, polyethylenes, polypropylenes, polystyrenes, polycarbonates, polyvinyl chlorides, polyvinylidene chlorides, polyesters, and saponified products of ethylene-vinyl acetate copolymers are suitable. When it is desired for the laminated material to have good lustre, polyamide, polymethyl methacrylate, etc. are selected. On the other hand, when it is

desired to obtain a matted surface, polypropylene, etc are selected.

Between layer C and layer D there may, if desired, be a coloured coating layer. This
5 coloured coating layer may be formed by coating the thermoplastic resin layer (D) with a coating material having the desired colour.

The thicknesses of the layers of the laminated material of the invention are not critical. A
10 suitable ratio would be layer A: modified polyolefin layer: layer B: layer C: layer D = 100-200: 5-30: 10-100: 0.03-0.08: 20-100.

To produce the laminated material of the
15 invention, the layers are bonded together by any suitable procedure. For example, in the case of dry lamination, an adhesive is coated, and in the case of extrusion lamination, a thin film of the above-described modified polyolefin, for example, is used.
20 In the former dry lamination, a suitable adhesive is selected from known adhesives. A suitable example is an epoxy resin-based adhesive.

When the laminated material of the invention is required to treat at high temperatures for the
25 purpose of, e.g., sterilization, a specific adhesive

for dry lamination is placed between the metal-vacuum deposited layer and the resin layer. Dry lamination adhesives which can be used include polyester or polyether-based polyurethane resins, and acrylic resins, such as acrylic acid alkyl ester and methacrylic acid alkyl ester. The amount of the adhesive coated is from 2 to 10 g/m² and preferably from 1.5 to 8 g/m².

Suitable solvents include aromatic hydrocarbons, esters, and halogen-containing hydrocarbons. The foregoing adhesive is coated between the vacuum deposited metallic layer and the resin layer by means of a dry laminator and dried and, thereafter, the two layers are laminated on each other to form the desired laminated material.

In producing the laminated material of the invention, it is preferred to employ a process in which a laminated material of layers A and B and a laminated material of layers C and D are previously produced, and the two laminated materials are then laminated on each other. In accordance with this process, it is possible to apply a vacuum deposition of a metal, e.g., aluminium, onto a thin film, which will lead to a great increase in productivity. The laminated material of the invention can be moulded

into containers and the like by techniques such as moulding under vacuum, and moulding under vacuum and pressure.

5 The laminated material of the invention possesses the decorative effect due to metallic lustre; by using a coloured coating layer in combination, there can be obtained a colour decorative effect. Since the laminated material of the invention is superior in gas barrier properties, 10 light-shielding properties, and moisture resistance, when it is used as a container, for example, the contents can be stored therein for a long period of time. Furthermore, since the container is less subject to breakdown or deformation and even if it 15 is deformed it can be easily restored, therefore, a reduction in product value does not occur. By suitably selecting the synthetic resin to be used in the laminated material, it becomes possible to apply a retort processing onto the resulting container. 20 With laminated materials in which the above-described adhesives are placed between the vacuum deposited metallic layer and the resin layer, heat resistance is superior and it is possible to apply a high temperature sterilizing treatment. In this case, the 25 vacuum deposited metallic layer is stable and is not

scattered. Accordingly, the laminated material of the invention is useful as a packaging material and particularly as a material for use in the production of food packaging containers.

5 The laminated material of the invention is illustrated in the drawings, of which:

 Figure 1 is a schematic view showing an embodiment of the laminated material of the invention;
10 and

 Figure 2 is a schematic view showing another embodiment of the laminated material of the invention.

 In the drawings, the reference numerals are as follows:

- 15 1 ... Transparent thermoplastic resin layer (layer D)
 2 ... Metal-vacuum deposited layer (layer C)
 3,3'... Polyolefin layer (layer A)
 4 ... Gas barrier resin layer (layer B)
20 5 ... Adhesive for dry lamination
 6 ... Coloured coating layer
 7 ... Modified polyolefin layer

 The invention is further illustrated by the following examples.

EXAMPLE 1

25 A coextrusion laminated sheet comprising a

polypropylene layer, a layer of polypropylene modified with maleic anhydride and a layer of saponified product of ethylene-vinyl acetate copolymer (ethylene content: 30 mole %) (thickness: 750 microns: 20 microns: 30 microns) was produced. A 30-micron thick nonstretched polypropylene film with a vacuum deposited aluminium layer provided on one surface thereof was laminated on the foregoing coextrusion laminated sheet through an epoxy resin-based adhesive with the vacuum deposited aluminium layer in contact with the ethylenevinyl acetate copolymer saponified product layer. The laminated material obtained had a metallic lustre.

EXAMPLE 2

A laminated material was produced as described in Example 1 except that there was used in a film produced by coating a nonstretched polypropylene film with a gold coating agent and vacuum-depositing aluminium on the coating layer. A container produced by vacuum thermal moulding of the above-produced laminated material did not have a surface lustre, but had a metallic feeling.

EXAMPLE 3

A laminated material was produced as described in Example 1 except that 6-nylon (relative viscosity:

4.4) was used in place of the ethylene-vinyl acetate copolymer saponified product.

EXAMPLE 4

5 A laminated material was produced as described in Example 1 except that polyethylene terephthalate (relative viscosity: 1.1) was used in place of the ethylene-vinyl acetate copolymer saponified product.

EXAMPLE 5

10 A laminated material was produced as described in Example 1 except that a nonstretched 6-nylon film was used in place of the nonstretched polypropylene film. A container produced by vacuum thermal moulding of the laminated material had surface lustre and a high quality feeling.

15 EXAMPLE 6

A 30-micron thick nonstretched polypropylene film was coated with a gold coating agent and, thereafter, aluminium was vacuum deposited on the coating layer. On the thus-treated polypropylene film was laminated, using an epoxy resin based adhesive, a coextrusion laminated sheet comprising a polypropylene layer, a layer of polypropylene modified with maleic anhydride, a layer of saponified product of an ethylene-vinyl acetate copolymer, a
20 layer of polypropylene modified with maleic anhydride
25

and a polypropylene layer (thickness: 350 microns:
20 microns: 30 microns: 20 microns: 350 microns)
with that the vacuum deposited aluminium layer in
contact with the polypropylene layer. A

5 container produced by vacuum thermal moulding of the
resultant laminated material did not have surface
lustre, but had a metallic feeling.

EXAMPLE 7

Aluminium was vacuum deposited on one side of a
10 25 micron thick nonstretched polypropylene film.
Separately, a coextrusion laminated sheet comprising
a polypropylene layer, a layer of polypropylene
modified with maleic anhydride and a layer of
saponified product of an ethylene-vinyl acetate
15 copolymer (ethylene content : 30 mole %; thickness:
750 microns: 20 microns: 30 microns) was produced.

A polyester-based polyurethane adhesive (resin
content: 25% by weight; viscosity: 50 centipoises
at 25°C; solvent: ethyl acetate) was coated on the
20 polypropylene film in an amount (calculated as resin)
of 5 g/m² by a dry laminator and dried. The adhesive
coated film was laminated on the coextrusion laminated
sheet so that the vacuum deposited aluminium
layer was in contact with the layer of the
25 saponified product of the ethylene-vinyl acetate

copolymer, which was then allowed to stand at 35°C for 10 hours to obtain a laminated material as shown in Figure 2.

5 The 180° peeling strength of the product at the adhesive surface was 850 g/15mm, and after application of retort sterilization at 120°C for 30 minutes, there were observed no changes in form, adhesive force, or in the vacuum deposited coating film.

EXAMPLE 8

10 A laminated material was produced as described in Example 7 except that a sheet comprising a polypropylene layer, a layer of polypropylene modified with maleic anhydride, a layer of a saponified product an of ethylene-vinyl acetate copolymer
15 (ethylene content: 30 mole %), a layer of polypropylene modified with maleic anhydride and a polypropylene layer (layer thickness: 350 microns: 20 microns: 30 microns: 20 microns: 350 microns) was used as the coextrusion laminated sheet. The 180° peeling
20 strength of the product at the adhesive surface was 820 g/15 mm, and after application of retort sterilization at 120°C for 30 minutes, there were observed no changes in form, adhesive force, or in the vacuum deposited layer.

EXAMPLE 9

A laminated material was produced as described in Example 8 except that a polyether-based polyurethane adhesive (resin content: 25% by weight; viscosity: 40 centipoises at 25°C; solvent: ethyl acetate) was used in an amount (calculated as resin) of 3 g/m² as the adhesive. The 180° peeling strength of the product at the adhesive surface was 680 g/15 mm and after application of retort sterilization at 120°C for 30 minutes, there were observed no changes in form, adhesive force, or in the vacuum deposited layer.

EXAMPLE 10

A laminated material was produced as described in Example 7 except that there was used a 25 micron thick nonstretched polypropylene film, on one surface of which had been provided a gold coloured coating and, thereafter, vacuum deposited aluminium. This laminated material had golden metallic lustre.

CLAIMS

1. A laminated material comprising: (A) a layer composed mainly of polyolefin; (B) a layer composed mainly of a saponified product of an ethylene-vinyl acetate copolymer, a polyamide resin or a polyester resin; (C) a vacuum deposited metallic layer; and (D) a layer composed mainly of a transparent thermoplastic resin.
2. A laminated material according to claim 1 characterized in that the layer A is composed of polypropylene, a copolymer of propylene and another α -olefin, a high density polyethylene, a medium density polyethylene or a low density polyethylene.
3. A laminated material according to claim 1 or claim 2 characterized in that the layer B is composed of a product resulting from the saponification of an ethylene-vinyl acetate copolymer having an ethylene content of from 25 to 50 mole percent to the extent that the degree of saponification is at least 93 percent.
4. A laminated material according to claim 1 or claim 2 characterized in that the layer B is composed of 6-nylon, 6,6-nylon, 6,10-nylon, 11-nylon or 12-nylon.
5. A laminated material according to claim 1 or

- or claim 2 characterized in that the layer B is composed of polyethylene terephthalate, a polyethylene terephthalate copolymer containing a saturated dibasic acid, a polyethylene
- 5 terephthalate copolymer containing a diol component or a mixture thereof.
6. A laminated material according to any preceding claim, characterized in that the layer C is a vacuum deposited aluminium layer.
- 10 7. A laminated material according to any preceding claim characterized in that the layer D is composed of polyamide, polymethyl methacrylate, polyethylene, polypropylene, polystyrene, polycarbonate, polyvinyl chloride, polyvinylidene chloride,
- 15 polyester or a saponified product of an ethylene-vinyl acetate copolymer.
8. A laminated material according to any preceding claim characterized in that a coloured coating layer is formed on the inner face (opposing
- 20 the layer C) of the layer D .

FIG. 1

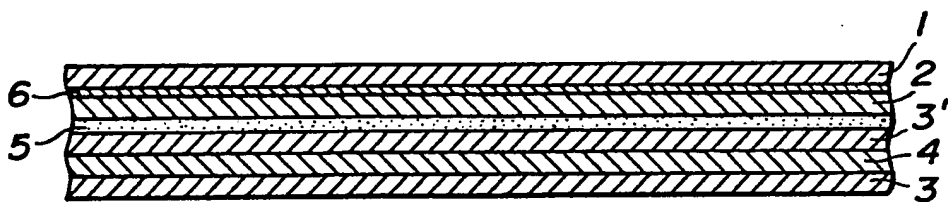
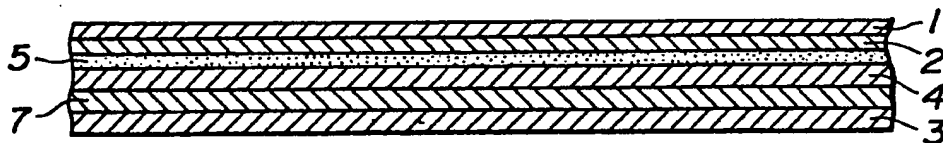


FIG. 2





European Patent
Office

EUROPEAN SEARCH REPORT

0096581

Application number

EP 83 30 3280

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 3)
X	DE-A-2 719 113 (K.H. SENGEWALD KG.) * Figures 2,5,8,9,10,14,16,17; claims 1-3, 6-8, 20,25; page 8, lines 15-21; page 10, lines 4-11; page 12, lines 1-20; page 16, lines 15-19; page 17; page 18 *	1,2,6-8	B 32 B 27/08
X	FR-A-2 228 610 (W.R. GRACE & CO.) * Claims 1-5; examples 1,6,8,11,12,13; pages 2,3,4 *	1-3,5-7	
X	GB-A-1 351 073 (SOCIETE D'ETUDES & D'EXPLOITATIONS TECHNIQUE) * Whole document *	1,2,5	
			TECHNICAL FIELDS SEARCHED (Int. Cl. 3)
			B 32 B
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 22-09-1983	Examiner DE LA MORINERIE B.M.
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			